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The University of Washington
Department of Chemistry

A Laboratory Study of Nitrogen Fixation by the High Tension Arc

by

PHILIP GORDON COLIN

A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of Doctor of Philosophy

Reprinted from the Journal of Physical Chemistry, Vol. XXXI, pp. 1539-1558, 1927

Seattle
University of Washington
1927

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A LABORATORY STUDY OF NITROGEN FIXATION BY THE HIGH TENSION ARC

Introduction

In previous work from this laboratory,[2] results have been reported on the influence of reduced pressure on the yield of fixed nitrogen from the high tension electric arc. The data were secured under conditions in which the velocity of the molecules of gas through the arc increased as the pressure was reduced. Results were also presented dealing with the equilibrium: $N_2 + O_2 = 2\,NO$; equilibrium being secured by passing the gases repeatedly through the arc at atmospheric pressure.

This investigation deals with (1) the effect of reduced pressure on the yield of fixed nitrogen with a constant velocity of the molecules of gas through the arc and (2) equilibria obtained in an arc with variation of conditions, such as pressure and composition of the initial gas.

Historical

The oxidation of nitrogen in an electric arc is a long known process and the literature has become quite voluminous. An extensive review will not be given. It will suffice to discuss briefly only that literature which has a direct relation to the experimental results presented herein.

(a) Effect of Pressure.

The investigations on the effect of pressure on the oxidation of nitrogen by means of the electric arc are not numerous. Haber and Holwech[3] used a small arc furnace of the Schönherr type for the study of the formation of nitric oxide in the high tension arc under pressure. The current was varied from 0.55 to 1.5 amperes, the power from 660 to 1650 watts and the gas flow from 2940 to 8700 liters per hour. The most favorable yield was 76 grams of nitric acid per kilowatt-hour at a pressure of two atmospheres, although the volume concentration was only 0.36 per cent.

Haber and his co-workers,[4] using an alternating current with small vertical arcs between electrodes of platinum, oxidized iron and Nernst filaments under a pressure of 100-150 mm. and with a slow circulation of gas (mixtures of N_2 and O_2) succeeded in obtaining a percentage by volume of 9.8%NO for air, with a current of 0.24 ampere at 5000 volts in the case of iron electrodes and 0.35 ampere at 3700 volts in the case of Nernst glower electrodes. For mixtures of equal volumes of N_2 and O_2 a yield of 14.4% and for mixtures of 81.7

[1] Du Pont Fellow in Chemistry at University of Washington 1924-1926.

[2] Tartar and Perkins: J. Phys. Chem., 30, 595-616 (1926).

[3] Haber and Holwech: Z. Elektrochem., 16, 810 (1910).

[4] Haber and Koenig: Z. Elektrochem., 13, 725 (1907); 14, 689 (1908); Haber, Koenig and Platou: 16, 789; Haber and Platou: 796 (1910).

parts O_2 and 18.3 parts of nitrogen 12.1% NO was obtained. The most efficient gas pressure was about 100 millimeters of mercury. With a direct current arc burning in a quartz tube a maximum concentration of 8.16% NO (by volume) was obtained at a pressure of 150 millimeters of mercury, with a current of 0.27 ampere at 1400 volts and with a gas velocity of 6 liters per second.

Morden[1] reports results showing a yield of approximately 90 grams of nitric acid per kilowatt-hour (concentration 1.5 to 2.5% NO by volume) at a pressure of 590 mm. of mercury. This was accomplished with a short direct current arc between a water cooled silver anode and an iridium cathode coated with calcium oxide: current 0.115 ampere at 240 volts, air velocity 43.7 liters per hour. The cathode was heated with a secondary current to stabilize the arc. Morden claims that heating the cathode does not affect the yield. Holwech[2] was able to practically duplicate Morden's results. Holwech and Koenig[3] continued the work with short, direct current arcs and secured a yield of 84 grams of nitric acid per kilowatt hour (concentration 2.3% NO by volume) at 500 mm. pressure, using an iron cathode and water cooled copper anode with a current of 0.2 ampere at 280 volts. The gases from the arc were drawn off through a water cooled capillary. Heating the cathode with a secondary current was found to be unnecessary. Attempts to use more energy in the arc gave smaller yields. Reversing the current and also using an alternating current were less successful.

Haber and Holwech[4] tried the use of a direct current arc at pressures greater than atmospheric. The arc was provided with a water cooled copper cathode and iron anode: the air was brought in tangentially at the bottom of the furnace in order to give a whirling motion to the arc. Currents varying from 0.55 to 1.5 amperes at 700 to 2075 volts were used with pressures varying from 2 to 21 atmospheres. The best yield was 76 grams of nitric acid (concentration 0.36% NO) per kilowatt hour at a pressure of 2 atmospheres. Increase of pressure was not found to be beneficial to yield.

Briner and Naville[5] made a study of the effect of pressure on the yield from alternating current arcs between wires of different metals (Fe, Ni, Pt, Ir, Zn) and employed various mixtures of nitrogen and oxygen. They found the yield to depend upon the nature of the electrode but that in each case a maximum yield was obtained using an excess of nitrogen at 700 mm. and 100 mm. pressure and a minimum at 500 mm. The yields were low, not greater than 20 grams of nitric acid per kilowatt hour.

The Nitrogen Products Committee (British)[6] state that "recent experimental work in Switzerland has shown that the yield of combined nitrogen from arc furnaces can be increased by more than 25 per cent by the addition

[1] Morden: Trans. Am. Electrochem. Soc., **14**, 133 (1908).
[2] Holwech: Z. Elektrochem., **16**, 369 (1910).
[3] Holwech and Koenig: Z. Elektrochem., **16**, 803 (1910).
[4] Haber and Holwech: Z. Elektrochem., **16**, 810 (1910).
[5] Briner and Naville: Helv. Chim. Acta **2**, 348 (1919); J. Chim. phys. **17**, 329 (1919).
[6] Final Report Nitrogen Products Committee, p. 241 (1920).

of 50 per cent of oxygen to the air supply and that a further increase of about 25 per cent is obtained if the furnace is operated under an absolute pressure of about half an atmosphere."

Data are not available covering equilibrium concentrations of nitric oxide obtained through a large current range and through a wide variation in reduced pressure for various mixtures of oxygen and nitrogen.

(b) Thermal vs. Electrical Equilibria.

For long the question has been in the minds of investigators in this field as to whether the reaction between nitrogen and oxygen in the electric arc is a typical reversible reaction conforming to the requirements of the law of mass action. The reader is referred to the resume given by Knox[1] of the literature prior to the year 1921. Suffice it to say that the work of Muthman and Hofer,[2] LeBlanc and Nuranen,[3] Grau and Russ,[4] Foerster,[5] and Lee and and Beyer,[6] with luminous arcs at ordinary pressures, indicated that this reaction is of a purely thermal nature and that the mass action law holds. Le Blanc and Nuranen and also Grau and Russ, used various mixtures of nitrogen and oxygen and obtained values for equilibrium constants which agreed fairly closely.

On the other hand, Warburg and Leithauser[7] and Berthelot[8] showed definitely that nitric oxide may be produced by the action of the silent discharge on air. Since the experiments were carried out at ordinary temperature, the formation of nitric oxide under these conditions was attributed to electrical influences. Haber and his co-workers,[9] sought to show by the use of cooled, high tension, alternating current arcs at reduced pressures that the primary action is an electrical one—that the kinetic energy of the gaseous ions and of the electrons in the arc is utilized directly in the production of NO and that an "electrical equilibrium" may be secured and to which the mass law does not apply. Haber and Koenig obtained at a pressure around 140 mm., a concentration of 9.8% NO from air, 12.1% from "invert air" (4 vols. oxygen and 1 vol. nitrogen) and 14.4% with a mixture of equal volumes of these gases. They believe that if the temperature of the arc becomes too great then the thermal influences obscure the primary electrical effect.

Only recently, Daniels, Keene and Manning[10] have made the following very important statement in regard to thermal and electrical equilibria of reactions in an electric discharge:

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[1] Knox: "Fixation of Atmospheric Nitrogen," 2d Edition (1921).

[2] Muthman and Hofer: Ber., **36**, 438 (1903).

[3] Le Blanc and Nuranen: Z. Elektrochem., **13**, 297 (1907).

[4] Grau and Russ: Z. Elektrochem., **13**, 345, 573 (1907).

[5] Foerster: Z. Elektrochem., **12**, 536 (1906).

[6] Lee and Beyer: Z. Elektrochem., **13**, 701 (1907).

[7] Warburg and Leithauser: Ann. Physik, **20**, 743 (1906); **23**, 209 (1907).

[8] Berthelot: Ann. Chim. Phys., (8) **9**, 145 (1906).

[9] Haber and Koenig: Z. Elektrochem., **13**, 725 (1907); **14**, 689 (1908); Haber, Koenig and Platou: **16**, 789; Haber and Platou: 796 (1910).

[10] Daniels, Keene and Manning: Trans. Am. Electrochem. Soc., **44**, 247 (1923).

"It is essential to register a strong reservation in regard to the use of the word 'temperature' as applied to an electrical discharge. Ames,[1] among others, has pointed out that one cannot speak properly of the temperature of a mass of distributed molecules of this kind. In an electrical discharge certain molecules acquire an electrical charge and are moved with high velocity in the electrostatic field. Free electrons are moved with still greater velocities. Other molecules in the path are ionized by collision and are given accelerated velocities by the field, so that regions of high kinetic energy result. This high velocity of the molecules and ions is equivalent to a high temperature, but the distribution of velocities does not follow Maxwell's distribution law. It is not possible then to ascribe a definite temperature to the discharge, or even to smaller regions within it, and much less to a single molecule or ion.

"The classical controversy as to whether the formation of nitric oxide in the arc is a purely thermal process or an electrical phenomenon becomes then superfluous. Qualitatively, it is proper to consider an arc as a region of high temperature, but thermodynamic calculations based on a definite temperaature determines the thermodynamic equilibrium of the gases which leave the arc. It is evident that the concentration of endothermic compounds in the electrical field, may be much greater but it cannot be calculated quantitatively because a definite temperature cannot be ascribed to it. Furthermore, it is of little practical importance anyway, for the products cannot be removed without going through this region of lower kinetic energy, where a real equilibrium with a lower concentration of the endothermic compounds is established. For calculations of equilibrium then the temperature should be that of the region immediately surrounding the electrical discharge, but outside of the electrical field. One can say then that an electrical equilibrium exists which gives a higher concentration of the products than the thermal equilibrium."

The above quotation has been given because it states clearly the point of view taken by the writers regarding the temperature of a high tension arc. No attempt will be made in this paper to ascribe a definite thermodynamic temperature within the electrical field of the arc.

Description of Apparatus

(A) Electrical Equipment

The source of power, transformer and electrical measuring instruments were the same as those used in previous work by Tartar and Perkins.[2]

(B) The Arc Furnaces

1. Furnace No. 1.

This furnace was the same as used in the former investigation. It was employed in making experiments on the yield of fixed nitrogen at reduced pressure and also in obtaining equilibria at atmospheric pressure.

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[1] Ames: Bull. Am. Inst. Min. and Met. Eng., p. 2482 (1919).

[2] Tartar and Perkins: J. Phys. Chem., 30, 395 (1926).

2. Furnaces No. 2, 3 and 4.

These furnaces were used in the study of equilibria. The first furnace used in preliminary experiments is shown in Fig. 1. The electrodes of heavy copper wire forming a "horngap," were tightly fitted into a rubber stopper which in turn was fitted to a forty liter carboy. The stopper was also provided with inlet and exhaust tubes. The arc formed was of a flaming type, starting at the point at which the electrodes were closest together, running up the electrodes and finally breaking, whereupon a new arc was started.

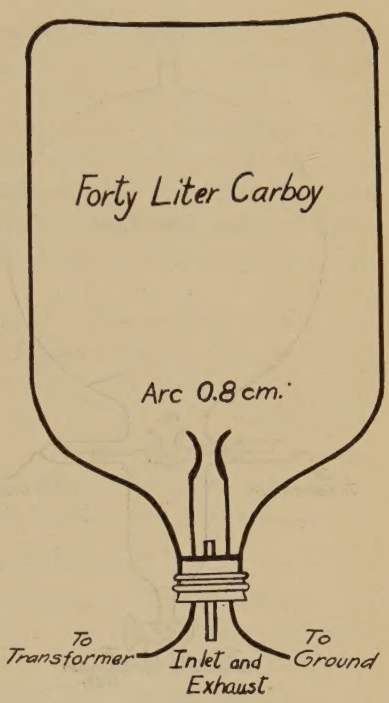

FIG. 1

Furnace No. 3 was similar in construction to that shown in Fig. 1, except that inlet and exhaust tubes were fitted into the neck of a five-liter flask through a rubber stopper. The "horngap" electrodes were nicrome wire and were sealed into the neck of the flask at a distance of about 0.8 cm. from each other. The burning arc was continuous, playing constantly between two points upon the electrodes.

Furnace No. 4 consisted of a five-liter Pyrex flask having platinum "horngap" electrodes sealed into the neck of the flask; see Fig. 2. The distance between the electrodes was about 0.8 cm. The neck of the flask was drawn out and sealed to a three way cock, connected to a manometer and to the apparatus for the absorption of the oxides of nitrogen. The tubulation in the bulb was connected to the gas supply and to a Cenco Hivac Pump, which served to obtain the desired pressures. This furnace was very satisfactory as it could be operated successfully over wide variations in pressure and in current.

(C). The Gas Apparatus and Method of Procedure.

The general arrangement of the gas apparatus used with Furnace No. 1 was the same as that used by Tartar and Perkins.[1]

The arced gases were sampled in different ways, namely: by vacuum flasks, by an adsorption train or in some few preliminary experiments when the sampling carboy was used for the furnace chamber itself (Fig. 1.)

The vacuum flasks or bottles were of a capacity of from 12 to 20 liters with narrow necks fitted with stoppers. The absorption train, consisted of six cylinders 3 cm. in diameter and 25 cm. high, each fitted with inlet and outlet tubes and connected in series with the furnace.

[1] Loc. cit. (See Figs. 2 and 3).

Vacuum flasks were used when the gas was passed but once through the arc at reduced pressure, a procedure which is here designated as "a direct run" at reduced pressure.

In other experiments, the gas was confined in a closed system and circulated repeatedly through the arc until equilibrium was reached, here designated as "a closed cycle run." A 12 to 20 liter bottle served as a gas reservoir and was connected in a closed circuit with the arc furnace, the flow meter and a small "Cenco" positive acting rotary pump. A tube containing phosphorus pentoxide was inserted into the circuit to remove any traces of water. The pump was equipped with a by-pass or shunt. By varying the rate of flow of the gas through the by-pass the desired velocity of the gas through the closed cycle was easily controlled.

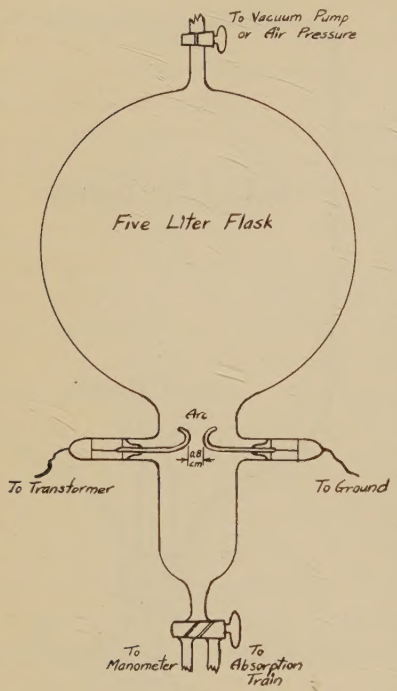

FIG. 2

The method for carrying out the direct runs at reduced pressure and the closed cycle runs at atmospheric pressure were the same as in the previous work.

Many experiments were performed in which equilibrium was reached with the gas at reduced pressure. These experiments will be referred to as "reduced pressure equilibrium runs." The furnace was evacuated to the desired pressure after the gas mixture (nitrogen and oxygen) had been introduced. When the gas mixture was not air, the arc furnace flask was evacuated to a calculated pressure and brought to atmospheric pressure by admitting oxygen and re-evacuating to the desired pressure. When equilibrium was reached (maximum concentration of NO in gas coming from the arc), the furnace and its contents were allowed to come to room temperature amd pressure and temperature readings were again taken. The gas in the furnace was then analyzed by passing the entire gas content through the absorption train.

Methods of Analysis

(a) Analysis of Samples taken with the Vacuum Flask.

The vacuum flasks were highly evacuated prior to taking the samples. The gas sample was taken over a considerable period of time in order to keep the pressure at the arc at the desired value. The temperature and barometric pressure were recorded. After the vacuum flask had been removed from the circuit, the pressure was allowed to come to atmospheric pressure, and water and a known volume of hydrogen peroxide solution were added. The vacuum

flask was then allowed to stand over night. Potassium hydroxide solution was then added and the entire contents of the flask was washed into a liter beaker, boiled to decompose the hydrogen peroxide, cooled and titrated with standard acid, using methyl red as the indicator. Analyses of samples taken with closed cycle runs at atmospheric pressure were made in a similar manner.

(b) Analysis of Solutions from the Absorption Train.

The first two towers were filled with a known volume of hydrogen peroxide solution (3%), and the last three with a known volume of standard alkali. This manner of filling the towers was found to be the most satisfactory as no "fogging" was produced. Absorption of nitrous gases in alkaline solutions of hydrogen peroxide was found to be difficult, while the method employed gave satisfactory results. Advantage was taken of the fact that hydrogen peroxide in dilute solution quantitatively oxidizes nitrous acid to nitric acid.[1] It was found that less than 10 per cent of the total absorption takes place in the last three towers.

At the conclusion of a run, the tower solutions were washed into a liter beaker, boiled to decompose the excess of hydrogen peroxide and made acid with standard acid. The beaker and its contents were then cooled, made alkaline by the addition of standard alkali, and titrated with standard sulfuric acid using methyl red as the indicator.

Litmus, methyl orange, and phenolphtalein are all decolorized by traces of nitrous acid but methyl red is only very slowly acted upon by this acid.[2]

Direct Runs at Reduced Pressure

Tartar and Perkins[3] showed that as the pressure in the arc furnace was reduced, there was a gradual reduction both in the concentration of nitric oxide produced and in yield of fixed nitrogen per kilowatt-hour. They employed a furnace which at atmospheric pressure gave the technical yield of 60 grams nitrogen (as nitric acid) per kilowatt-hour with a constant gas flow of 200-250 liters per hour. For a given rate of gas flow, (calculated to standard conditions) the velocity of the particles through the arc chamber increased with the reduction in pressure. At a pressure of 150 mm., the particles were swept through the furnace at a velocity nearly five times as great as when the same quantity of gas was passed through at 760 mm.

Consequently a series of experiments were made reducing the rate of flow of gas through the arc as the pressure was diminished in order to keep the velocity of the particles of gas through the arc constant.

These runs were made in the following manner: two stopcocks were inserted in the gas line; one immediately before the arc furnace and the second after the exit. The tube from the second stopcock was connected to a large capacity vacuum pump. By careful adjustment of the stopcocks, the rate of flow of gas and the pressure were easily controlled.

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[1] Baeyer and Villiger: Ber., **34**, 755-62 (1901).

[2] Koehler, Marqueyrol and Jovinet: Ann. Chim. anal., **18**, 45 (1913).

[3] Tartar and Perkins: J. Phys. Chem., **30**, 595 (1926).

Samples of the gas were taken at the exit of the furnace by the vacuum flask method, employing large bottles of 12 to 20 liters capacity provided with tightly fitting stoppers. Large flasks were necessary in order to secure sufficient quantity of gas for analysis. The bottles were thoroughly dried, evacuated to a small fraction of a millimeter of pressure and then connected to the gas line. The stopcock was then opened slowly and the gas permitted to flow in until the pressure within the bottle was the same as that in the arc furnace. The temperature and pressure at time of sampling were recorded.

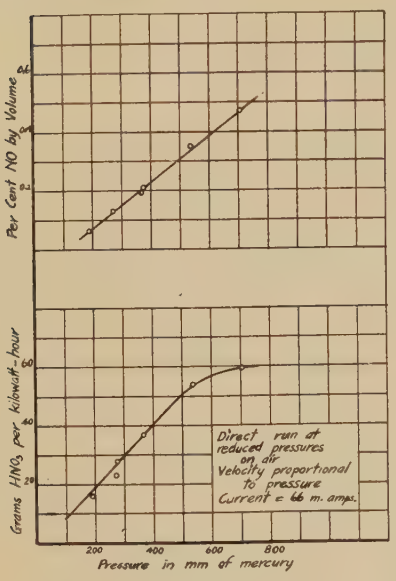

FIG. 3

The experimental data for the reduced pressure runs are reported in Table I and graphically represented in Fig. 3.

These results show that there was a gradual decrease both in the concentration of the nitric oxide and in the yield per kilowatt-hour as the pressure was reduced. As will be shown later, it is possible to build up very high concentrations of nitric oxide at reduced pressures but *no results were obtained indicating that a decrease in pressure may be utilized for securing a greater efficiency in yield by the arc process.*

TABLE I

Results of Direct Runs at Reduced Pressures

Exp. No.	At Electrodes		Watts Corrected for Transformer losses	Velocity of gas thru arc. (Liters per hr. std. Cond.)	Pressure in Arc Chamber (mm. of Hg.)	Nitric Oxide (Percent by volume).	Nitric Acid (HNO_3) (gms. per kw.-hr.)
	Current in Milliamperes.	Approx. Voltage					
8 a	66.4	1900	77.3	356.8	706	0.47	59.6
4 a	65	1510	59	258	535	0.35	53.7
7 a	67	1250	50	171.9	371	0.21	37.3
5 a	65.5	1225	47	177.8	366	0.19	36.9
11 a	66.2	1030	44	129.1	273	0.13	27.7
9 a	67	870	38.6	96.3	271	0.13	22.8
6 a	67.8	800	36.3	86.7	188	0.063	15.8

Equilibrium Runs with Air at Atmospheric Pressure without Circulation of Gases

A series of runs was made with air in order to determine the effect of current upon the equilibrium concentration of nitric oxide produced in the electric arc without circulation of the gas other than that caused by the variation in temperature in different parts of the system. The apparatus is shown in

Fig. 1. The arc produced was similar to the type used in the Pauling process for nitrogen fixation; running up the horn-gap and breaking, whereupon a new arc was started at the point at which the electrodes were closest together. Copper electrodes were used.

Runs were made as follows: The carboy was thoroughly dried and the stopper and electrodes inserted. It was then evacuated, filled with conditioned air and the arc was started. Barometric pressure and temperature readings were taken at the beginning and end of the runs. When equilibrium had finally been attained, the arc was stopped and the carboy and contents allowed to come to room temperature. Water and a known volume of hydrogen peroxide solution (3%) were then admitted, the electrodes removed and the carboy was allowed to stand overnight. Standard potassium hydroxide solution was then added, the contents of the carboy was washed into a liter beaker, the solution boiled to decompose the excess hydrogen peroxide and titrated with standard acid using methyl red as the indicator.

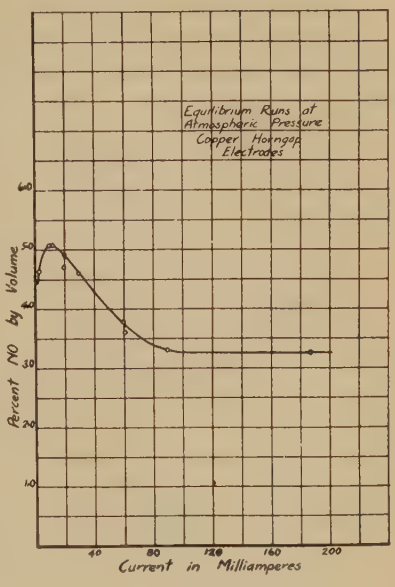

Fig. 4

The experimental data secured from these equilibrium runs at atmospheric pressure are reported in Table II and graphically represented in Fig. 4.

Table II

Equilibrium Runs with Air at Atmospheric Pressure

Exp. No.	Secondary Current (In Milliamperes)	Per Cent Nitric Oxide (By Volume)	Exp. No.	Secondary Current (In Milliamperes)	Per Cent Nitric Oxide (By Volume)
13 b	3	4.64	10 b	31	4.64
9 b	10	5.08	11 b	61	3.79
7 b	12	5.08	5 b	61	3.61
8 b	20	4.92	1 b	88	3.30
12 b	20	4.69	2 b	90	3.28
14 b	30	4.55	3 b	92	3.36
6 b	30	4.6	15 b	187	3.26

It will be noted that a maximum concentration of nitric oxide of about 5.1 per cent was produced with a current of 10 to 12 milliamperes and the concentration decresaed for both increases and decreases in the value of the current. For lower values of current the arc was not able to build up this concentration and for higher values apparently the temperature gradient from the arc was decreased so that this higher concentration was lessened

by the thermal effects of the arc. The same equilibrium concentration was obtained for values of current above 90 milliamperes, indicating that the temperature gradient for the higher current arcs was the same.

Closed Cycle Runs with Air at Atmospheric Pressure

In the preceding set of experiments a maximum concentration of nitric oxide was produced with the furnace gas in a comparatively static condition, the only motion of the gases being due to the rise of the hot gases from the arc. The next set of experiments was undertaken to show maximum concentration which could be built up with gases passing through the arc with considerable velocity. Equilibrium was attained by passing the gases continuously around a closed sytem composed of the Furnace No. 1, large sample bottle, pump as used by Tartar and Perkins.[1]

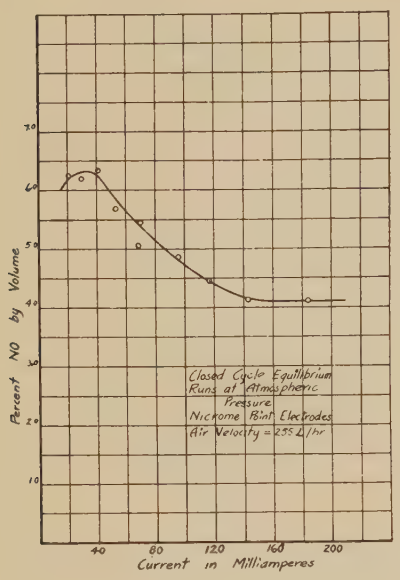
Percent NO by Volume
Current in Milliamperes
Closed Cycle Equilibrium Runs at Atmospheric Pressure
Nicrome Pint Electrodes
Air Velocity = 255 L/hr

FIG. 5

The arc played between points of nicrome wire. The velocity of the gas through the furnace was 255 liters per hour. Runs were made as follows: The dried sample bottle filled with conditioned air was connected into the system and the circulating pump started. The by-pass valve was then adjusted to give the desired gas velocity and the arc was then started. Readings of barometric pressure and room temperature were taken. When equilibrium had been attained the sample bottle was removed and the contents analyzed.

Very erratic results were obtained at first due to the presence of traces of moisture in the system. This was remedied by inserting a long tube in the closed cycle system containing phosphorus pentoxide. The experimental results are arranged in Table III and presented graphically in Fig. 5.

As in the previous set of experiments the maximum concentration was produced with a small value of current (about 30 milliamperes), decreasing with increase and decrease of current. For high values of current the concentration was again constant.

Another set of closed cycle experiments utilizing electrodes of nicrome formed into a horn-gap, (See Fig. 6) and a gas velocity of 113 liters per hour, gave results very similar to the preceding set, except that somewhat lower concentrations were obtained. These results are also recorded in Table III and in Fig. 7.

The results given in Tables II, III show that the equilibrium concentration of nitric oxide was dependent both upon the current and the ve-

[1] Loc. cit.

TABLE III

Closed Cycle Runs with Air at Atmospheric Pressure

Exp. No.	At Electrodes			Velocity of gas thru arc. Liters per hr.	Nitric Oxide Per Cent by volume
	Current In Milli-amperes	Approx. Voltage	Wats Corrected for Trans-former losses		
9 E	21.0	1920	30.5	255	6.24
8 E	30.0	1430	33	"	6.18
4 E	41.5	2050	68	"	6.34
5 E	53.2	1990	86.5	"	5.68
3 E	68	1920	108.5	"	5.04
2 E	70	1650	98	"	5.46
1 E	95	1420	116.5	"	4.85
6 E	117	1700	161	"	4.44
7 E	143	1830	211	"	4.12
10 E	185	1480	194	"	4.10
17 F	5	—	24	113	2.84
19 F	5	—	24	"	3.24
18 F	7	—	31.5	"	2.93
20 F	10	—	34	"	3.66
15 F	13	4460	35	"	4.01
9 F	20.5	2020	21.5	"	3.61
13 F	28	2300	37	"	5.62
7 F	28	2230	34.5	"	5.95
6 F	40	1910	50	"	4.40
14 F	40	2140	55	"	4.92
10 F	41	1610	41	"	5.14
8 F	50.5	1930	61.5	"	4.69
2 F	62	1770	74	"	4.11
11 F	72	1800	86	"	4.06
1 F	91	1850	113	"	3.80
3 F	116	1410	111	"	3.68
4 F	145	1400	137	"	3.48
12 F	170	2270	258	"	3.34

locity of the gas through the furnace. The higher concentration obtained by circulating the gas was due evidently to a steeper temperature gradient just outside the arc which gave less opportunity for the decomposition of nitric oxide. The concentrations of NO with the quietly burning, "static" arc with current 100-200 milliamperes were about the same as obtained by Tartar and Perkins[1] for equilibrium with a small whirling arc of the Schönherr type and an air velocity of 200 to 600 liters per hour.

[1] Loc. cit.

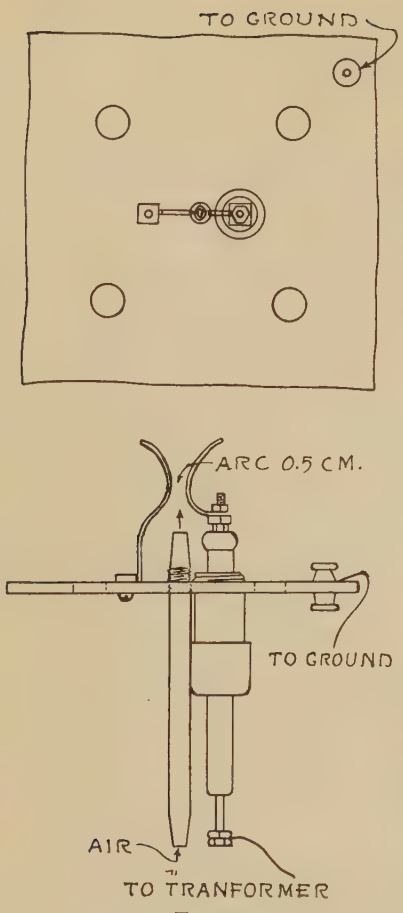

FIG. 6

Equilibrium Runs at Reduced Pressures

The furnaces previously used were not satisfactory for determining equilibrium at reduced pressures due to the fact that a high vacuum could not be maintained over a considerable length of time. Furnace No. 3 was made for preliminary work. It consisted of nicrome horn-gap electrodes sealed into the neck of a five-liter Pyrex flask fitted with a rubber stopper holding inlet and outlet tubes. The inlet reached to the bottom of the flask, so that the contents could be readily blown out into the absorption train. The stopper was covered with sealing wax in order to maintain the vacuum. The rubber exposed to the oxides of nitrogen was not affected in the absence of moisture.

In these preliminary runs, air was the only gas mixture used. The furnace chamber was evacuated to the desired pressure and the arc started. Barometric pressure and room temperature readings were taken at the start and finish of the run. At the conclusion of the run, the furnace was allowed to come to the temperature of the room, dry air was introduced to bring the pressure to atmospheric and

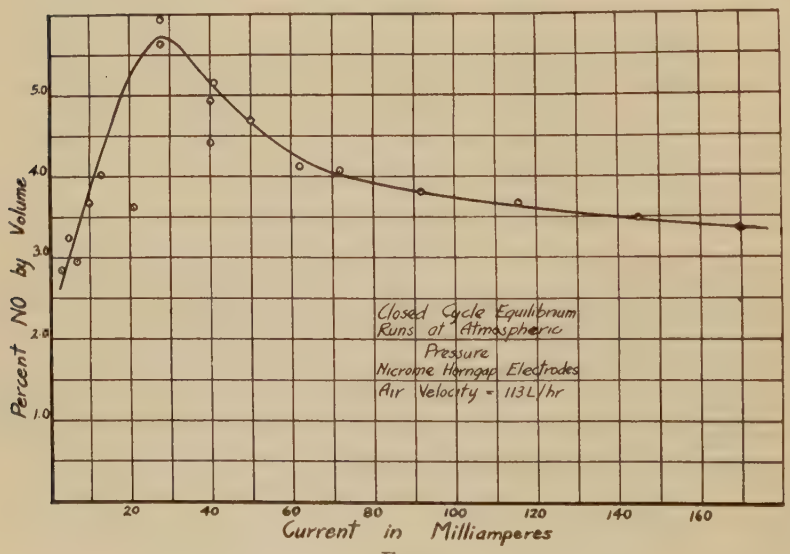

FIG. 7

the gas content was then blown through the absorption train. Two series of runs were made namely for currents of 39 and 66 milliamperes. The experimental data are arranged in Table IV and shown graphically in Fig. 8.

TABLE IV

Equilibrium Runs with Air at Reduced Pressure

Exp. No.	At Electrodes			Arc Pressure mm. of Hg.	Nitric Oxide Per cent by volume
	Current in Milli-amperes.	Approx. Voltage	Watts Corrected for trans-former losses		
10 I	40	390	13.5	119	3.93
2 I	38.7	410	13.5	160	4.92
7 I	40.3	430	15	189	5.40
5 I	38.7	430	14	200	5.71
8 I	40.1	460	15.5	251	6.45
6 I	39	490	16	346	7.03
3 I	39.2	510	16.5	392	6.11
4 I	38.8	520	16.5	401	6.78
1 I	38.8	610	20	561	6.07
6 J	66	390	22	106	3.97
5 J	66.5	410	23	141	5.26
7 J	65	420	23.5	198	6.61
8 J	66	430	24.5	287	7.60
9 J	65.7	460	26	406	7.50
10 J	65.7	500	28	476	6.96
11 J	64.6	540	30	591	6.57
12 J	65	580	32.5	733	5.6

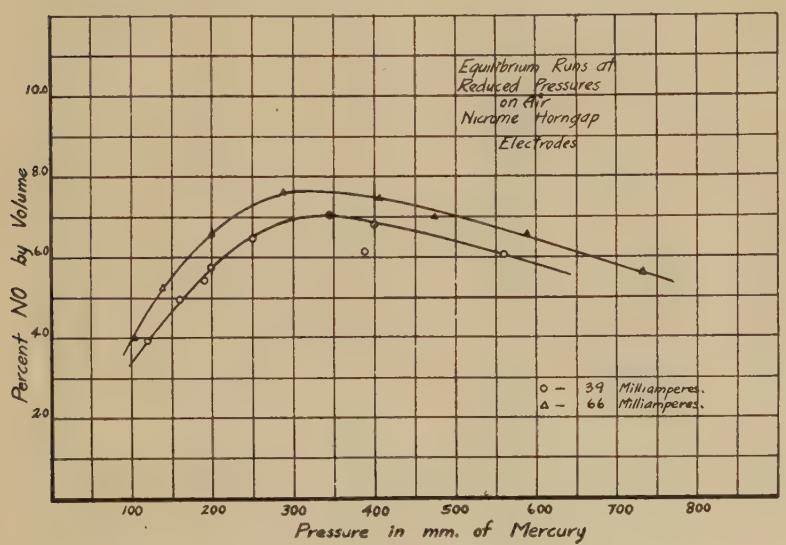

FIG. 8

It is readily seen that a higher concentration of NO by volume was obtained at the higher current value and at a lower pressure.

Furnace No. 4 (Fig. 2) was then constructed in order to more accurately investigate the various factors influencing the obtainable concentration of NO from the arc.

Runs were made as in the previous set of experiments except that mixtures other than air were used. In the latter case the furnace chamber was evacuated to the calculated pressure, brought to atmospheric pressure by admitting dried oxygen, and re-evacuated to the desired pressure. This method insured the same mixture of initial gases.

Series of runs were made upon air with currents of 39, 65, 92, 126, 156 and 190 milliamperes; upon invert air (4 vols. of oxygen and 1 vol. of nitrogen) with currents strengths of 39, 92, and 190 milliamperes and upon a 50-50 nitrogen-oxygen mixture with current strengths of 92 and 190 milliamperes. These runs were made with increasing value of current in order to determine the maximum concentration which could be produced by the arc used. The experimental data are recorded in Tables V, VI and VII and represented graphically, in Figs. 9, 10, and 11.

TABLE V

Equilibrium Runs with Air at Reduced Pressures: Current 39 to 190 Milliamperes

Exp. No.	At Electrodes			Arc Pressure, in mm. of Hg.	Nitric Oxide Per cent by Volume
	Current in Milliamperes	Approx. Voltage	Watts Corrected for Transformer losses		
2 M	39.0	490	16	162	5.22
8 M	39.0	530	17.5	195	5.37
10 M	39.1	540	18	200	5.62
12 M	39.3	570	19	210	5.64
11 M	39.0	650	21.5	255	6.31
1 M	39.5	620	20.5	259	6.69
13 M	39.5	720	22	294	6.39
6 M	39.0	730	22.5	294	6.57
4 M	39.0	740	24.5	354	6.42
7 M	38.8	770	24.5	409	6.11
9 M	39.3	840	26.5	480	5.68
5 M	38.9	960	29.5	540	5.37
3 M	38.0	1060	32.5	612	4.86
1 L	62	370	20	71	5.28
17 L	63	390	21.5	96	5.34
11 L	64	410	22.5	114	4.91
2 L	62	460	24.5	163	6.12
3 L	63	520	28	264	6.91
8 L	62	530	28	267	7.23
14 L	64	590	32	343	6.45

TABLE V (continued)

Exp. No.	At Electrodes			Arc Pressure in mm. of Hg.	Nitric Oxide Per cent by Volume
	Current in Milli-amperes	Approx. Voltage	Watts. Corrected for Trans-former losses		
12 L	62.5	600	31.5	368	6.30
15 L	64	630	34	419	5.95
13 L	63	640	33.5	429	5.70
16 L	62.5	670	35	462	5.94
9 L	62.5	660	34	474	5.98
10 L	62.5	720	37	573	5.46
7 L	62	730	37.5	634	5.00
8 K	94	410	33	71	5.88
7 K	91	430	32.5	103	5.93
10 K	90	470	34.8	155	6.94
9 K	91	500	37.5	206	7.56
13 K	91	500	38	216	7.30
11 K	92	530	40	253	7.04
3 K	92	550	42	288	6.54
12 K	90	570	43	365	6.06
4 K	91	600	45.5	406	5.68
5 K	92	610	47	473	5.41
6 K	92	670	50.5	602	5.12
7 Q	126	480	48	77	7.58
6 Q	127	500	52	110	7.98
5 Q	127	520	53	146	8.28
8 Q	128	540	55	171	7.92
4 Q	126	540	55	197	7.63
1 Q	126	590	61	287	6.10
2 Q	126	620	65	353	5.54
3 Q	126	660	68	469	5.11
5 R	156	510	62	58	8.06
3 R	154	520	61	93	8.64
6 R	156	510	62.5	94	8.36
7 R	156	540	65.5	124	8.16
2 R	154	540	65.5	140	8.15
4 R	156	550	68.5	161	8.05
3 S	188	510	73	73	8.15
5 S	189	520	76	88	8.26
2 S	192	530	78	94	8.79
4 S	186	520	74	96	8.69
9 S	191	560	81	124	8.22
1 S	185	540	76	127	8.35
7 S	188	550	80	135	8.35

TABLE VI

Equilibrium Runs with Invert Air: Current 39, 92 and 190 Milliamperes

Exp. No.	At Electrodes			Arc Pressure in mm of Hg.	Nitric Oxide Per cent by Volume
	Current In Milliamperes	Approx. Voltage	Watts Corrected For Transformer losses		
9 O	40.6	420	14.5	104	5.82
7 O	40.6	470	16	150	7.94
6 O	40.0	500	16.5	193	8.20
10 O	40.3	650	22	223	7.93
8 O	40.0	600	21	238	7.56
5 O	39.7	680	23	261	7.45
4 O	40.1	740	25	319	6.70
1 O	39.3	800	27.5	390	6.13
3 O	38.4	830	27	450	5.94
8 N	93	420	32	92	7.94
11 N	92.5	460	35	126	8.93
2 N	92	470	35.5	159	8.77
9 N	93	480	38	176	8.62
10 N	92.5	490	37.5	184	8.92
6 N	93	500	38.5	209	8.71
4 N	95	520	42.5	251	7.81
7 N	93	540	43.5	308	6.94
1 N	91	590	45.5	399	6.09
3 N	92	640	50	472	5.90
5 N	93	670	54	568	5.31
1 U	186	525	75	96	12.27
2 U	190	525	76	99	12.1
3 U	188	540	78	124	11.1
4 U	192	520	77	74	11.0

An examination of the curves shown in Fig. 9 shows that the pressure at which a maximum concentration of NO was obtained was variable and dependent upon the current through the arc. For a current of 39 milliamperes the maximum concentration was obtained at a pressure of about 320 mm., for 65 milliamperes at about 260 mm., for 92 milliamperes at about 210 mm., for 126 millamperes at about 150 mm. and for 190 millamperes at 100 mm. of mercury. Moreover the equilibrium concentration increased with the increase of current until a value of 8.8 per cent NO by volume was obtained. This was the maximum concentration attainable with the arc.

Fig. 10 shows that for the higher pressure both air and invert air gave about the same concentration but below a pressure of 350 mm. of mercury this was no longer true. If the law of mass action is applicable to the reaction

$$N^2 + O_2 = 2\,NO$$

air and invert air should have given the same equilibrium concentration.

Apparently the law is approximately valid for the higher pressures that is, where thermal properties predominate in the arc.

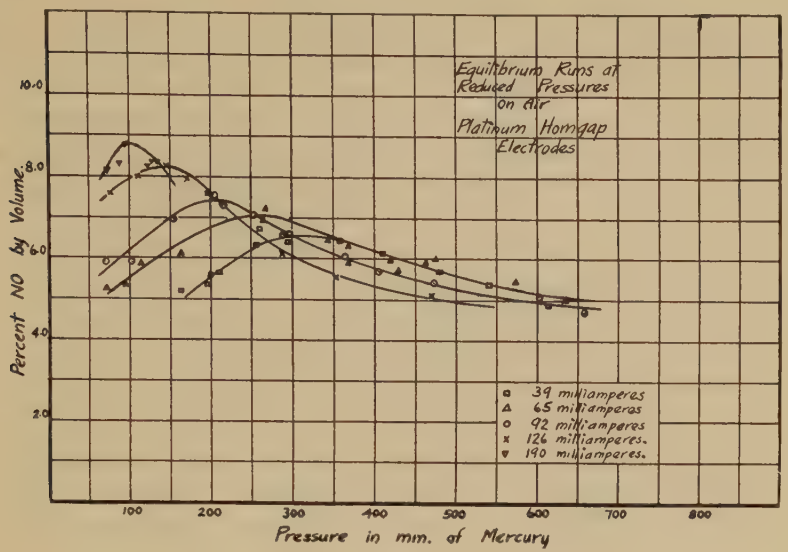

FIG. 9

TABLE VII

Equilibrium Runs with Mixture of Equal Volumes of Nitrogen and Oxygen

Exp. No.	At Electrodes			Arc Pressure mm of Hg.	Nitric Oxide Per cent by Volume
	Current In Milli-amperes	Approx. Voltage	Watts Corrected For Trans-former losses		
8 P	93.5	460	36	109	11.66
9 P	93	480	36.5	129	11.91
6 P	94	490	38.5	156	12.51
11 P	92.5	490	37.5	155	11.94
10 P	92	490	37.5	174	11.6
2 P	93	550	43	257	9.19
7 P	93	610	48	364	7.39
4 P	92.5	660	51.5	463	6.75
5 P	92	750	59	587	5.91
3 T	190	520	76	72	12.39
1 T	188	520	74	97	13.0
2 T	185	540	76	109	12.62
4 T	189	540	78	100	13.17

In Fig. 11, equilibrium concentrations of NO are represented for the three gaseous mixtures employed namely: air, invert air, and equal volumes of oxygen and nitrogen. The law of mass action would require that the equal

volume mixture should give a concentration of 25% in excess of that of air or invert air. This was approximately true at the higher pressures, but at the reduced pressures the deviation was marked.

The results secured within the pressure range 100-150 mm. are in general accord with the findings of Haber and Koenig.[1]

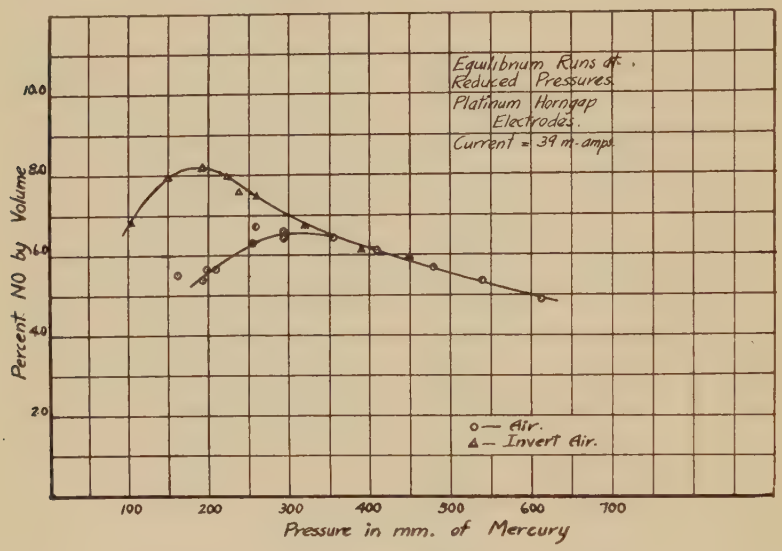

FIG. 10

The data on the equilibria obtained with air and invert air may be used to give an idea regarding the temperature gradient and the rapidity of cooling at the edge of an arc without artificial circulation of the gas. Approximately six per cent of nitric oxide (see Tables V and VI and Figs. 10 and 11) was formed with both air and invert air at half an atmosphere using currents of 39 and 92 milliamperes. This concentration of NO was evidently in thermal equilibrium with the gas immediately outside the arc filament at the particular temperature at which the equilibrium was "frozen." By extrapolation from their experiemental data, Nernst, Finckh and Jellinek[2] estimate that the temperature corresponding to a thermal equilibrium concentration of six per cent NO is approximately 3500° Abs. The velocity of the decomposition of nitric oxide has been investigated by Jellinek[3] for the temperature range 689° to 1750° C. From this reaction constant and the equilibrium constant of the reaction, the reaction constant for the formation of nitric oxide can be determined. From these data the rates of formation and decomposition of NO in a given mixture can be calculated.[4]

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[1] Loc. cit.

[2] Nernst, Finckh and Jellinek: Z. anorg. Chem., **45**, 111, 126 (1905); **49**, 213, 229 (1906).

[3] Jellinek: Z. anorg. Chem., **49**, 263 (1906).

[4] For details concerning the formulation and method of calculation the reader is referred pp. 134, Bulletin 2041, U. S. War Dept.; Report on the Fixation and Utilization of Nitrogen.

The estimated time required for the decomposition at 3500° Abs. of 40 per cent of the nitric oxide present in an air mixture containing initially twice the amount of this substance that will be present when equilibrium is established, is 1.1×10^{-8} seconds. At 1900° and 1770° Abs. the times required for this amount of decomposition are 2.5 and 21 minutes respectively. The gas from the arc zone should surely be cooled very quickly to at least 1900° Abs. to "freeze" the equilibrium. Below this temperature the rate of decomposition will be sufficiently slow that the gas may be cooled less rapidly without appreciable loss of combined nitrogen. These values indicate that in order to

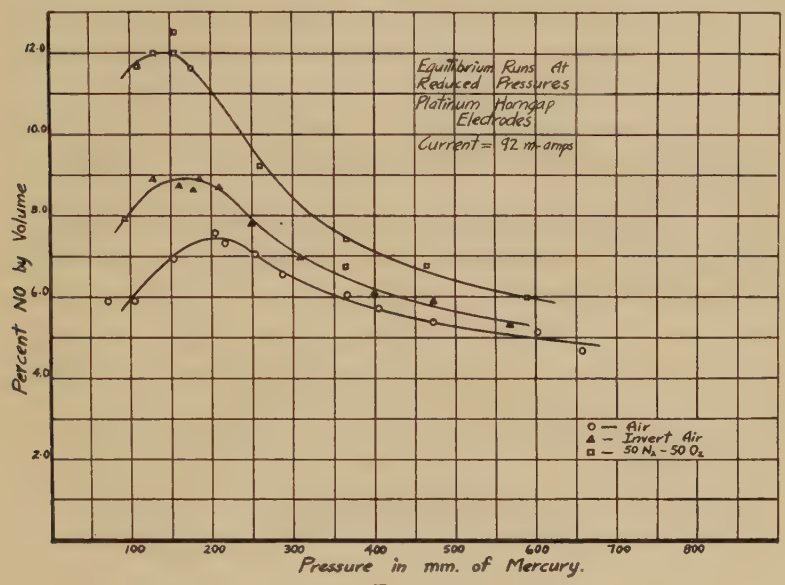

FIG. 11

"freeze" the equilibrium in the gases coming from the arc at 3500° Abs. there must be an abrupt drop in temperature within an extremely short distance of about 1600°. Also that even from a quietly burning arc the equilibrium is "frozen" with a rapidity that is almost incredible. The writer realizes that the reaction velocities given above were obtained by extrapolation from experimental data secured at lower temperatures. Nevertheless, the conclusion seems justified at least when gases are passed through the arc with considerable velocity the approximate equilibrium concentration of nitric oxide at the high temperature in the immediate vicinity of the arc is secured without appreciable decomposition. Furthermore, the rapidity with which the equilibrium is "frozen" shows the futility of the efforts of previous investigators to increase the concentration of nitric oxide by bringing the gases after leaving the arc in contact with water-cooled walls.

Acknowledgment

Grateful acknowledgment is made to the E. I. du Pont de Nemours Company for the grant of a fellowship which made this investigation possible.

Summary

1. The use of reduced pressure gave a decrease both in the concentration of nitric oxide and in yield of fixed nitrogen per kilowatt hour.

2. The maximum equilibrium concentration of nitric oxide obtained over a wide range in pressure was dependent upon the current.

3. The effect upon the equilibrium concentration of nitric oxide produced by varying the velocity of the gases was not marked.

4. High concentrations of nitric oxide may be produced in an uncooled high tension, electric arc at reduced pressure.

5. The maximum concentrations of 8.8 per cent for air, 12.2 per cent for invert air and 13.1 per cent for equal volumes of oxygen and nitrogen were obtained at a pressure of about 100 mm. of mercury.

6. The law of mass action holds approximately for the reaction between nitrogen and oxygen in the high tension electric arc at pressures greater than one-half atmosphere.

7. Water-cooling of the gases after leaving the arc is unnecessary.

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